

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### NO DRAWINGS

### Method of Polymerizing Fluoroolefins in Aqueous Medium

We, DAIKIN KOGYO KABUSHIKI KAISHA, a Japanese Body Corporate of Shin-hankyu Building, 8 Umeda, Kita-ku, Osaka-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the polymerization of fluoroolefins in aqueous media without the use of conventional polymerization initiators. More particularly, the invention pertains to said method of polymerization mainly comprising subjecting the starting materials to irradiation of ionizing radiations.

According to the method employed in the prior art, fluoroolefins are polymerized in aqueous media in the presence of a dispersant, such as water-soluble anionic surface active agents having a polyfluorinated alkyl group, and a polymerization initiator, such as persulfates or water-soluble peroxides, employed singly or in admixture with a reducing agent, such as sodium sulfite.

According to the above method, however, it takes more than several tens of hours to prepare a colloidal polymer dispersion of a polymer concentration of 30 percent by weight or thereabout. The resultant polymer dispersion being unstable, said method is almost confined to the batch system, and the transportation of the resultant products is not easy. Complicated concentration procedures are further to be applied in order to prepare a dispersion of higher concentrations, since it is impracticable for said method to prepare a dispersion of concentrations of more than 40 percent by weight in a single polymerization procedure because of the unstability of the resultant products.

An object of the present invention is accordingly to provide a method wherein

polymer dispersions having a high order of concentrations can be obtained within a 45 very short period of reaction.

Another object of the invention is to provide a method wherein the resultant polymer dispersion is provided with a high order of stability, so that there can be obtained a polymer dispersion of concentrations of from 40 to 60 percent by weight in a single polymerization procedure and the conventional concentration procedure is eliminated or can be carried out quite easily.

The present invention resides primarily in the discovery that fluoroolefins can be markedly activated and the polymerization thereof takes place quite easily even without the use of conventional polymerization initiators when subjected at least at the initial stage of reaction to irradiation of ionizing radiations; and in the discovery that the average particle size of the polymers present in the resultant dispersions is relatively small and the stability of said polymer dispersions is much improved as compared with that of the conventional polymer dispersions, producing a polymer dispersion of concentrations of from 40 to 60 percent by weight or thereabout in a single polymerization procedure. Transportation can thus be much facilitated and the reaction system can be subjected to a continuous flow system.

Thus according to the present invention there is provided a method of polymerizing fluoroolefins in aqueous media, comprising subjecting the reaction system to irradiation of ionizing radiations in the absence of oxygen at a temperature ranging from 0° to 100°C. under a pressure of from 1 to 100 kg/cm<sup>2</sup> in the presence of from 0.001 to 10% by weight of a water-soluble anionic surface active agent having a water solubility of at least 0.001 percent by weight at 100°C.

and having a polyfluorinated alkyl group having from 4 to 13 carbon atoms, the atoms bonded to said carbon atoms being selected from H, F and Cl, and at least 1/2 the bonded atoms being F.

The ionizing radiations employed in the present invention are electromagnetic waves, such as  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, X-rays, electron rays, neutron rays, proton rays and 10 deuteron rays, and high-energy ion beams of various sorts. Most desirable results are obtained with  $\gamma$ -rays in particular.

The aforesaid radiations may be applied to the reaction system either at the initial 15 stage of reaction or throughout the entire period of reaction.

When the radiations are applied at the initial stage of reaction, in more detail, the reaction system is allowed to continue to 20 react by utilizing the resultant post-polymerization ability lasting for a considerable period of time. The advantages of this method are, firstly, that said method produces a polymer dispersion of many excellent mechanical and dielectric properties, 25 preventing degradation in qualities induced by a continuous irradiation; secondly, that said method and stability of resultant polymer dispersion renders it possible to subject 35 the reaction system to a continuous flow system, producing a uniform polymer dispersion under simplified procedure and effective use of radiation sources; and thirdly, that said method enables control of the dimension of the resultant polymer particles, because the post-polymerization procedure 30 following the interruption of irradiation allows the particles to grow substantially in dimension in proportion to the period of post-polymerization without substantial increase in number. 40

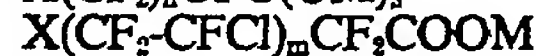
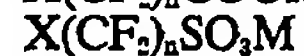
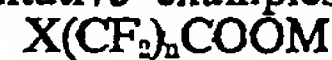
The application of radiations throughout the entire period of reaction, on the other hand, is particularly effective for obtaining a 45 polymer dispersion of a relatively high order of stability. For said application enables the resultant particles to increase in number without substantial growth in dimension, whereby a polymer dispersion of relatively 50 minute particles can be obtained.

When the application of radiations is confined to the initial stage of reaction, the irradiation is continued until the resultant polymer concentration reaches at least 5 55 weight percent, preferably from 10 to 30 weight percent. In this case, the dose rate to be applied ranges from  $1 \times 10^2$  to  $1 \times 10^8$  r/hr, preferably from  $5 \times 10^2$  to  $1 \times 10^7$  r/hr. When the radiations are applied throughout 60 the entire reaction period, the irradiation dose rate should not exceed  $1 \times 10^8$  r/hr, preferably to from  $5 \times 10^2$  to  $1 \times 10^7$  r/hr to prevent the resultant polymers from degradation in properties. In any case, the 65 total dose to be applied ranges from

$1 \times 10^3$  to  $1 \times 10^8$  r, preferably to from  $1 \times 10^3$  to  $1 \times 10^7$  r.

The starting fluoroolefins employed in the present invention are vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, octafluorocyclobutane, trifluorochloroethylene, and the like. Said materials are employed either singly or in admixture with one another or with one of the other olefinically unsaturated compounds such as 75 vinyl chloride, hexafluoropropene and perfluorovinyl ethers and the like. The most desirable embodiment are 100 to 70 : 0 to 30 polymer or copolymer dispersions of tetrafluoroethylene and hexafluoropropene. 80 Said homopolymer or copolymer can be obtained by polymerizing the mixture of tetrafluoroethylene and hexafluoropropene in the weight ratio of 1 : 0 to 15.

The dispersants employed in the present 85 invention are anionic surface active agents having a water solubility of at least 0.001 weight percent at 100°C. and having a polyfluorinated alkyl group having from 4 to 13 carbon atoms, the atoms bonded to said 90 carbon atoms being selected from H, F and Cl, and at least 1/2 the bonded atoms being F. Representative examples are:



wherein X is hydrogen or fluorine or chlorine; M is an alkali metal or  $-NH_4$  or  $-NR_2$ , R being hydrogen or alkyl having from 1 to 6 carbon atoms; n is an integer from 6 to 12 inclusive; m is an integer from 2 to 6 inclusive; and y is also an integer from 4 to 105 6 inclusive; comprising, for instance, water-soluble salts of polyfluoroaliphatic carboxylic acids, water-soluble salts of polyfluoroaliphatic sulfonic acids, water-soluble salts of sulfates of polyfluoroaliphatic alcohols; 110 water-soluble salts of phosphates of polyfluoroaliphatic alcohols; water-soluble salts of polyfluoropolychloroaliphatic carboxylic acids, and the like. These materials are employed 115 either singly or in admixture in the order of from 0.001 to 10 weight percent, preferably from 0.05 to 5 weight percent, in relation to the aqueous medium used. In admixture with said materials, further, there may be 120 employed in a slight amount a conventional dispersant, such as water-soluble salts of sulphates of aliphatic alcohols, water-soluble salts of phosphates of aliphatic alcohols, water-soluble salts of aliphatic sulfonic acids 125 or water-soluble salts of aromatic sulfonic acids.

The present invention rests further in the discovery that the reaction system is completely protected from polymerization in the 130

gas phase, producing a marked increase in the polymerization rate in the aqueous reaction system itself when the reaction is carried out in the presence of at least one species of saturated aliphatic hydrocarbons which are liquid under the polymerization conditions. Such hydrocarbons as specified can be properly selected from the group of butane, heptane, hexane, cyclohexane, dodecane, hexadecane, paraffin wax and the like. In order to prevent polymerization in the gas phase and formation of non-dispersible solid polymers, said hydrocarbons are effectively employed in such a small order of 0.5 weight percent or thereabout in relation to the aqueous medium employed. In order to prevent polymerization in the gas phase and to accelerate polymerization reaction in the aqueous reaction system itself, said hydrocarbons are employed in the order of at least 2 weight percent, preferably within the range of 2 to 20 weight percent from the economic points of view, in relation to the aqueous medium employed, although an increase in the hydrocarbons employed does not induce any bad effects on the polymerization reaction itself and the resultant polymers, preferable results being obtained with said hydrocarbons employed in the order of from 3 to 10 weight percent in relation to the aqueous medium employed. When, for instance, hexadecane is added in the order of 6 weight percent to the aqueous medium, the polymerization reaction takes place as rapid as 2 times the reaction where hexadecane is employed in the order of 1 weight percent, and as rapid as from several 10's to 200 times the reaction where the conventional water-soluble polymerization initiator is employed in the place of irradiation of ionizing radiations.

Of the aforespecified hydrocarbons, those hydrocarbons having more than 12 carbon atoms are employed in the prior art as a polymer dispersion stabilizer. In the present invention, however, the aforespecified hydrocarbons are employed not as stabilizing agent but as an agent to prevent polymerization in the gas phase and to accelerate polymerization reaction in the aqueous reaction system itself. Accordingly, those hydrocarbons having less than 11 carbon atoms inclusive and which could not be employed in the prior art because of their property to inhibit polymerization of fluoroolefins can be employed in the present invention for said purposes, insofar as said agents are liquid under the polymerization conditions.

In the present invention, there is no need of employing conventional stabilizers, since the average size of the particles of the resultant polymers are so minute and uniform in dimension that the resultant dispersion is markedly stable even without the use of

conventional stabilizers, although there may be added as a stabilizer those hydrocarbons having more than 12 carbon atoms or saturated halohydrocarbons such as trifluorotrichloroethane or tetrafluorodichloroethane.

The polymerization reaction of the present invention is carried out in the absence of oxygen at a temperature ranging from 0° to 100°C. under a pressure from 1 kg/cm<sup>2</sup> to 100 kg/cm<sup>2</sup>, preferably at from 5° to 80°C. under 3 to 50 kg/cm<sup>2</sup>.

In the present invention, furthermore, the reaction system can be subjected not only to the conventional batch system but to a continuous flow system. According to the latter system, the starting materials are continuously supplied into an autoclave under constant irradiation of ionizing radiations, while the reaction system reaching at least a 5 weight percent polymer concentration is being transferred into the other autoclave to continue to react by means of the post-polymerization ability of the reaction system, said supply of starting materials being carried out simultaneously with the transfer of the irradiated reaction system and in proportion to the amount transferred, and the pressure in said autoclaves being maintained at a constant level by means of fluoroolefins being supplied. The end product is drawn out of the system during the course of the polymerization reaction. Thus the reaction is carried out without interruption from the beginning to the end.

Preferred examples of the present invention are as follows, which are illustrative only and in which all parts are by weight:

#### Example 1

In a 1.5-liter stainless steel autoclave having a stirrer were placed 2.4 parts of ammonium perfluorooctanoate in 800 parts of deionized water. The vessel was evacuated to remove air and pressured to 10 kg/cm<sup>2</sup> with tetrafluoroethylene. The reaction system was then subjected under a 500 r.p.m. agitation at 25°C to  $\gamma$  irradiation of  $8 \times 10^4$  r/hr emitting from a 2,000-curie Co<sup>60</sup>. In the course of polymerization, tetrafluoroethylene was constantly supplied to maintain the decreasing pressure to 10 kg/cm<sup>2</sup>. The radiation source was removed 2 hours after application, allowing the polymerization reaction to continue for further 2 hours. The resultant dispersion was of a polymer concentration of 28.5 weight percent.

#### Example 2

In a 1.5-liter stainless steel autoclave having a stirrer were placed 2.4 parts of ammonium perfluorooctanoate and 8 parts of hexadecane in 800 parts of deionized water. The vessel was evacuated to remove air and pressured to 6 kg/cm<sup>2</sup> with tetrafluoroethylene. The reaction system was then



subjected under a 500 r.p.m. agitation at 25°C. to  $\gamma$  irradiation  $8 \times 10^4$  r/hr emitting from a 2,000-curie  $\text{Co}^{60}$ . Tetrafluoroethylene was constantly supplied to maintain the decreasing pressure to 6 kg/cm<sup>2</sup>. The radiation source was removed 1 hour after application, allowing the polymerization reaction to continue for further 1 hour. The resultant dispersion was of a polymer concentration of 35.9 weight percent, and the standard specific gravity of the polymers was 2.2300. Almost no polymerization took place in the gas phase.

The end product was concentrated to the order of 60 weight percent. 10 milliliters of the resultant dispersion were placed in a test tube, 13 mm in internal diameter, and rotated for 10 minutes at 3,000 r.p.m. The total amount of the precipitated polymers was no more than 1/3 that of the polymer dispersions prepared in accord with the conventional method where  $\text{K}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_3$  was employed as an initiator and concentrated to said order of 60 weight percent.

#### Example 3

Tetrafluoroethylene was polymerized with a mixture of 2.4 parts of ammonium perfluorooctanoate and 8 parts of hexadecane in 800 parts of deionized water in the same manners as described in Example 2, except the polymerization reaction was terminated with the interruption of irradiation applied for 1 hour, producing a dispersion of a polymer concentration of 24.6 weight percent.

#### Example 4

Tetrafluoroethylene was polymerized with a mixture of 2.4 parts of ammonium perfluorooctanoate and 40 parts of hexadecane in 800 parts of deionized water in the same manners as described in Example 2, producing a dispersion of a polymer concentration of 52 weight percent. The standard specific gravity of the resultant polymers was 2.2290. The polymerization reaction proceeded as rapid as 1.5 times that of Example 2 where hexadecane was employed in the order of 8 parts.

#### Example 5

Tetrafluoroethylene was polymerized with a mixture of 2.4 parts of ammonium perfluorooctanoate and 40 parts of hexadecane in 800 parts of deionized water in the same manners as described in Example 2, except the polymerization reaction was terminated with the interruption of irradiation applied for 1 hour, producing a dispersion of a polymer concentration of 35.5 weight percent.

#### Example 6

Tetrafluoroethylene was polymerized with a mixture of 24 parts of trifluorotrichloroethane and 4 parts of dodecane in 800 parts of deionized water in the same manners as described in Example 2, producing a dis-

persion of a polymer concentration of 34.4 weight percent. The standard specific gravity of the resultant polymers was 2.2255. Almost no polymerization took place in the gas phase.

#### Example 7

A mixture of 98 weight percent of tetrafluoroethylene and 2 weight percent of hexafluoropropene was polymerized in the same manners as described in Example 2, except agitation was applied at 1,000 r.p.m., producing a dispersion of a polymer concentration of 48 weight percent. Almost no polymerization took place in the gas phase. The amount of coagulation was also quite negligible despite the rapid agitation as specified.

#### Example 8

In a 10-liter stainless steel autoclave having a stirrer were placed 0.015 part of ammonium perfluorooctanoate and 0.15 part of n-cetane in 5 parts of deionized water. The vessel was evacuated to remove air and pressured to 6 kg/cm<sup>2</sup> with tetrafluoroethylene. The reaction system was then subjected under a 400 r.p.m. agitation at 20°C. to  $\gamma$  irradiation of  $3 \times 10^4$  r/hr emitting from a 2,000-curie  $\text{Co}^{60}$ , allowing to polymerize for 1 hour to the order of a polymer concentration of 20 weight percent, fresh tetrafluoroethylene being supplied to maintain the decreasing pressure to a constant level of 6 kg/cm<sup>2</sup>. The reaction system was then transferred at a flow rate of 5.5 l/hr into the other autoclave of the same type as described above, allowing the transferred reaction system to continue to polymerize for further 1 hour under a 400 r.p.m. agitation. Simultaneously, the starting materials of the above composition was being supplied at the flow ratio of 5 l/hr into the autoclave under irradiation to maintain the surface of the reaction system to a constant level, fresh portions of tetrafluoroethylene being further supplied to maintain the decreasing pressure in both of said autoclaves to a constant level of 6 kg/cm<sup>2</sup>. The end product was evacuated out of the system at a flow rate of 6.1 l/hr producing a dispersion of a polymer concentration of 33.3 weight percent.

#### WHAT WE CLAIM IS:—

1. Method of polymerizing fluoroolefins in aqueous media, comprising subjecting the reaction system to irradiation of ionizing radiations in the absence of oxygen at a temperature ranging from 0° to 100°C. under a pressure of from 1 to 100 kg/cm<sup>2</sup> in the presence of from 0.001 to 10% by weight of a water-soluble anionic surface active agent having a water solubility of at least 0.001 percent by weight at 100°C. and having a polyfluorinated alkyl group having from 4 to 13 carbon atoms, the atoms bonded to said carbon atoms being selected from H, F and Cl, and at least 1/2 the

bonded atoms being F.

2. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein said irradiation is applied in a dose rate ranging from  $1 \times 10^2$  to  $1 \times 10^8$  r/hr, the total dose being confined to from  $1 \times 10^3$  to  $1 \times 10^8$  r, to such an extent where the polymer concentration of the reaction system reaches at least 5 weight percent, and then the reaction system is allowed to continue to polymerize without application of radiations.

3. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein said irradiation is applied throughout the reaction period in a dose rate ranging from  $1 \times 10^2$  to  $1 \times 10^8$  r/hr, the total dose being confined to from  $1 \times 10^3$  to  $1 \times 10^8$  r.

4. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein the polymerization is carried out under a flow system, comprising continuously supplying the starting materials into a reaction vessel under irradiation, and continuously transferring the irradiated reaction system into the other reaction vessel to continue to polymerize without irradiation, the surface of the reaction system under irradiation being maintained at a constant level by means of the starting materials being supplied, the pressure in both of the reaction vessels being maintained at a constant level by means of fluoroolefins being supplied, the polymer concentration of the reaction system under irradiation being maintained at least 5 weight percent, and the end product being constantly drawn out of the system.

5. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein polymerization reaction temperature is from  $5^\circ$  to  $80^\circ\text{C}$ .

6. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein the pressure is from 3 to 50 kg/cm<sup>2</sup>.

7. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein a saturated aliphatic hydrocarbon is added in the order of at least 0.5 weight percent in relation to the aqueous medium being employed, said saturated aliphatic hydrocarbon being liquid under the polymerization conditions.

8. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein a saturated aliphatic hydrocarbon is added in the order of from 2 to 20 weight percent in relation to the aqueous medium being employed, said saturated aliphatic hydrocarbon being liquid under the polymerization conditions.

9. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein said water-soluble anionic surface active agent is added in the order of from 0.001 to 10 weight percent in relation to the aqueous medium being employed.

10. The method of polymerizing fluoroolefins in aqueous media as claimed in Claim 1, wherein hexafluoropropene is employed in a weight ratio from 0 to 15 in relation to and in admixture with tetrafluoroethylene.

11. The fluoroolefin polymer dispersions obtained in accord with the method as claimed in Claim 1.

12. The polymer powders obtained from the polymer dispersions prepared in accord with the method as claimed in Claim 1.

13. Method of polymerizing fluoroolefins in aqueous medium substantially as set forth in any one of Examples 1 to 8 herein.

14. Method of copolymerizing fluoroolefines with other olefinically unsaturated compounds in the manner set forth in Claim 1.

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